THE DEVELOPMENT OF MATERIALS
FOR STRUCTURES AND RADIATION SHIELDING IN AEROSPACE

SUMMARY OF RESEARCH

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Introduction

Polymeric materials on space vehicles and high-altitude aircraft will be exposed to highly penetrating radiations. These radiations come from solar flares and galactic cosmic rays (GCR). Radiation from solar flares consists primarily of protons with energies less than 1 GeV. On the other hand, GCR consist of nuclei with energies as high as 10^{10} GeV. Over 90% of the nuclei in GCR are protons and alpha particles, however there is a small but significant component of particles with atomic numbers greater than ten[1]. Particles with high atomic number (Z) and high energy interact with very high specific ionization and thus represent a serious hazard for humans and electronic equipment on a spacecraft or on high-altitude commercial aircraft (most importantly for crew members who would have long exposures). Neutrons generated by reactions with the high energy particles also represent a hazard both for humans and electronic equipment[2,3].

In addition, polymeric materials in space or at high altitudes suffer degradation from ultraviolet (UV) radiation, particularly from the high energy or vacuum ultraviolet (VUV) component[4]. Thus, for long-term use in these environments, polymeric materials must be UV resistant.

Materials exposed to the low earth orbit (LEO) are subjected to additional degradation by atomic oxygen (AO). The AO concentration in the LEO varies from 10^6 to 10^9 atoms cm^{-3} depending among other things on the distance above the earth, the latitude, and the solar cycle. Thus, a satellite in the LEO with a typical speed of 8 km s^{-1} will undergo 10^{12} to 10^{15} collisions cm^{-2} s^{-1} of AO with its forward facing surfaces. Because of its high reactivity, atomic oxygen causes surface erosion on polymeric materials.

The work on this project was focused in three areas: materials for GCR shielding, UV-resistant materials, and AO.-resistant materials.

Materials for GCR Shielding

Cosmic ray interactions in the upper atmosphere produce an annual radiation dose of 36 rem at the earth's surface[5], though virtually no primary cosmic rays reach the surface. The cosmic ray dose increases at higher elevations so that a person flying in an airplane at 32,000 ft receives an additional 0.5 millirem every hour[2]. This could become a significant problem for flights on future high-speed commercial aircraft which are anticipated to fly at about 70,000 ft. This could be particularly acute for crew members of such aircraft. Of course, persons flying beyond the earth's magnetic fields in deep space would be exposed to primary GCRs with only the material of the space vehicle itself for protection.

Galactic cosmic rays (GCR) contain a small but significant component of particles with high charge (Z ≥26) and high energy (E > 100 GeV)[1]. These so-called HZE particles interact with very high specific ionization and thus represent a serious hazard for humans and electronic equipment on high altitude aircraft and space vehicles. Calculations have shown that HZE particles have a strong preference for interaction with light nuclei[6]. Thus, hydrogen-containing polymers make the most effective practical shields. However, neutrons are formed in the interactions of these HZE particles with materials. Being uncharged, neutrons can only lose energy by collisions or reactions with a nucleus, a process that is much less probable than the Coulombic interactions of charged particles. Consequently, neutrons will migrate far from the site of the reaction in which they were formed. This increases the probability of neutrons reaching humans or electronic equipment. Fast neutrons (> 1 MeV) can interact with the silicon of such equipment resulting in the production of recoil ions which can cause single event upsets (SEU) in sensitive components[7]. Neutrons lose energy most effectively by elastic collisions with hydrogen atoms. Thus, hydrogen-containing polymers are not only effective in interacting with HZE particles, they are also effective in reducing the energy of the neutrons formed in the interactions.

Low-energy neutrons can be absorbed by nuclei in a process known as neutron capture. The products of such reactions are very often radioactive thereby increasing the risk of radiation exposure in humans. Two light elements, lithium and boron, each have a stable isotope which has a very large probability or cross section for absorbing low-energy neutrons. Boron is the better of the two, however, because its neutron-absorbing isotope, ^{10}B, has a neutron capture cross section four times greater than the corresponding lithium isotope, ^6Li. Also, the natural percentage of ^{10}B is 19.9% while that of ^6Li is only 7.5%, so that overall, natural boron is more than ten times as effective in absorbing neutrons as natural lithium. In addition, one of the products of neutron capture in lithium is radioactive tritium, while neutron capture in boron produces stable ^4He and ^7Li, both of which are readily absorbed into the material. Thus, a material containing both hydrogen and boron would be an effective GCR shield. The hydrogen atoms interact with the GCR ions and reduce the energy of the neutrons produced, thereby enhancing neutron capture by the boron.

We made specimens of two high performance polyimides, PETI-5, a thermoset material developed at the NASA Langley Research Center (LaRC), and K3B, a thermoplastic developed by DuPont. PETI-5 is commercially available from Imitec, and K3B is available from Fiberite. Boron was added either as 325 mesh amorphous powder (99.99%) or as boron carbide whiskers 300 microns long and 5 to 8 microns in diameter. Samples of each material were made as the pure polymer, the polymer with 10 and 20% amorphous boron powder, and the polymer with 10 and 20% boron carbide whiskers. Specimens were cut for compression, flexural, and tensile testing. The compression tests for PETI-5 showed that the addition of 20% boron carbide whiskers increased the compressive yield strength by about 9% over that of the pure material, while the addition of 20% amorphous boron powder decreased the compressive yield strength by more than 28%[8]. These results are shown in Figure 1. For K3B, the compression tests revealed that the addition of 10% boron carbide whiskers did not change the compressive yield strength, but addition of 20% boron powder caused a 25% reduction. These results are shown in Figure 2.

The addition of amorphous boron or boron carbide whiskers to PETI-5 lowered the tensile strength relative to that of the pure material. The addition of 20% boron carbide whiskers caused a 33% lowering while the addition of 20% amorphous boron caused a lowering of nearly 60%. On the other hand, addition of 10% boron carbide whiskers to K3B increases the tensile strength by about 50%over that of the pure material, while the addition of 20% amorphous boron powder caused a reduction of about 20% [9]. The tensile results for both polymers are shown in Figure 3. Flexural tests show results similar to those of the tensile tests. The addition of 10% boron carbide whiskers to PETI-5 results in no change to the maximum fiber strength from that of the pure material, while the samples with 20% boron powder showed a decrease of about 50%. However, the addition of 10% boron carbide whiskers to K3B caused the maximum fiber strength to increase by more than 50% over that of the pure material, while the value decreased by 27% when 20% boron powder was added [9]. The results of the flexural tests are shown in Figure 4. Flexural tests on a cured sample of K3B made by DuPont was compared to tests on the samples made in our laboratory. As seen in Figure 4, this sample had a maximum fiber stress about twice as high as our samples. The cure cycle supplied by DuPont was used in our laboratory, but clearly our samples were not as good. However, even the DuPont sample had a much lower maximum fiber stress than our PETI-5 samples. We also measured the glass transition temperature (T_g) using dynamic mechanical analysis (DMA). The addition of the boron additives has little effect on the T_g for either polymer, though the addition of 20% amorphous boron powder to PETI-5 appears to increase T_g slightly. The DMA results are shown in Figure 5. Measurements were also made on the samples using thremogravimetric analysis (TGA) and thermomechanical analysis (TMA). Results from TGA show that the addition of amorphous boron powder raises the average temperature for 5% mass loss as shown in Figure 6 for PETI-5. The softening temperature, T_s, measured by TMA also increases with the addition of amorphous boron powder as shown in Figure7, also for PETI-5. The TGA and TMA results for K3B showed similar trends.

Neutron shield studies were performed on K3B and K3B with 15% amorphous boron powder using a 3 curie PuBe neutron source at Virginia State University. Two samples 0.75 x 0.75 x 0.15 inches were clamped together with a piece of indium foil about 0.70 x 0.70 x 0.002 inches sandwiched between. The specimen was then inserted into the neutron source for 1.5 hours in order to produce ^{116}In which is a β^- emitter with a 54 minute half life. The background radiation of the room was counted during the activation process. Counts of the activated In foil were taken for one minute intervals every five minutes for at least one hour after the irradiation on an end-window Geiger counter. The counting results plotted as ln activity vs time are shown in Figure 8. The initial activity was calculated from a linear regression using the data points. A comparison of the initial activity when the foil is surrounded with pure K3B to that when the foil is surrounded with K3B/15% boron powder reveals that over 90% of the neutrons are absorbed in the boron-containing material.

UV Resistant Materials

Materials for aeronautic and space applications must be able to withstand ultraviolet (UV) radiation and sustained elevated temperatures. Polymeric materials are attractive for space applications because of their light weight, chemical stability, and good mechanical properties. Aromatic polyimides are particularly attractive because they have high glass transition

temperatures and possess thermal and thermooxidative stability at elevated temperatures[10]. Three polyimides were used in this study, two thermoplastics and one thermoset. All were studied as the neat resin and as composites with IM7 carbon fibers. Two of the materials were developed at the NASA Langley Research Center. One of these, called LARC™-8515, is a thermoplastic from the reaction of 3,3',4,4'-biphenyltetracarboxylic dianhydride and an 85:15 molar ratio of 3,4'-oxydianiline and 1,3-bis(3-aminophenoxy)benzene[10]. The second material, PETI-5, is a thermoset from the same reaction as that for LARC™ -8515 with the addition of a 4-phenylethynlphthalic anhydride endcapper. This material crosslinks during curing through interactions of the phenyethynyl groups[11]. The third material, K3B, was developed by DuPont and is a thermoplastic polyimide whose structure is proprietary.

Samples of all materials were fastened to an aluminum plate which was placed in a vacuum chamber. The pressure in the chamber was maintained around 100 millitorr and the plate was heated to 177°C. The samples were exposed to UV radiation which was transmitted through a quartz window from an external xenon UV lamp. The irradiations were done so that the irradiation time multiplied by the UV intensity was a constant as shown in Table 1. After exposure, the specimens were stored in airtight plastic bags until they were analyzed.

Table 1

Exposure time (h)	Intensity
500	1 sun
250	2 suns
167	3 suns

The exposed samples and controls were analyzed by DMA, TGA, TMA, x-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM). Surface analysis techniques (XPS and AFM) revealed changes due to UV exposure, while those techniques measuring bulk properties (DMA, TGA, and TMA) showed no changes due to the UV exposure. This conclusion is not surprising since the UV radiation is absorbed at the surface of the sample. Figure 9 shows a comparison of the carbon 1s peak measured by XPS for LARC™-8515 control and a sample exposed for 500 hours at 1 sun. The small peak at 288.6 eV seen in the control is characteristic of a carbon atom in a carbonyl group. The peak has disappeared after exposure, implying that carbonyl groups on the surface have been destroyed by the UV radiation. This same phenomenon is observed for the other thermoplastic, K3B, but is not observed for the thermoset, PETI-5. This may be a result of more mobility of the polymer chains in the thermoplastics than in the thermoset. Atomic force microscopy shows the surface of the exposed samples to be rougher than that of the control. This is shown in Figure 10.

AO Resistant Materials

This cooperative agreement was granted a special extension in order to analyze the specimens which were exposed on the Mir space station as part of the Optical Properties Monitor (OPM) experiment. Retrieval of the specimens was delayed because of problems which occurred on Mir while they were deployed.

We have found an organotin compound, bis(triphenyltin) oxide (BTO), which has an unusually high solubility in solutions of a number of commercial high performance polymers. Films of these polymers containing BTO showed a substantial reduction in erosion by atomic oxygen when compared with films of the pure material. Analysis has shown that in the presence of atomic oxygen, erosion of the exposed surfaces of the BTO-containing films leaves a residual protective tin oxide coating[12]. Since the additive is uniformly distributed throughout the polymeric material, any break or puncture in the protective coating is "healed" by the material below.

The primary objective of the OPM experiment was to study the natural and induced effect of the space environment on optical, thermal control, and other materials. The OPM was a multifunctional in-space optical laboratory in which four properties of flight samples could be measured: spectral total hemispherical reflectance from 250 to 2500 nm, vacuum ultraviolet (VUV) reflectance and transmittance from 121.6 to 250 nm, total integrated scatter (TIS) at 532 and 1064 nm, and calorimetric determination of total emittance and solar absorbance.

Samples were arranged on half of a circular carousel in four concentric rows. Instruments were positioned above or below the other half of the circle. A drawing of the OPM assembly is shown in Figure 11. We had three samples in the outer row each 0.75 inches in diameter and 1 mil thick. All were Ultem, a polyetherimide made by General Electric. One of the samples was pure Ultem, one contained 10% BTO by mass, and the third had 20 mass percent BTO. On a weekly basis, the carousel was to be rotated so that measurements could be made on each sample. Our samples were to have VUV measurements. Data from the measurements were to be collected by the crew and sent to earth by the Mir telemetry system.

Unfortunately, an unmanned cargo ship collided with Mir while the OPM experiment was deployed. As a result, power to the station was cut off for a period of time. This severely compromised the interactive part of the experiment, though the specimens were still exposed to the space environment. Thus, to date, no VUV data have been sent to us although we have been able to analyze the specimens.

The OPM specimens behaved in a manner similar to the other specimens exposed in space which we have analyzed. The specimen containing 20% BTO had the lowest percent mass loss while the pure Ultem had the highest. Table 2 shows the mass loss results.

Table 2

Sample	Mass Loss (mg)	% Mass Loss
Pure Ultem	0.33	1.67
Ultem/10% BTO	0.32	1.42
Ultem/20% BTO	0.19	1.04

Surface analysis by XPS showed that tin and oxygen dramatically increase on the surface after space exposure of the BTO-containing films. This is shown in Table 3 where the XPS data from the control and space exposed Ultem/20% BTO films are compared. Fortunately, little contamination appears on the surface of the exposed specimens in spite of the collision.

Table 3
Ultem with 20% BTO

Element	Atom % - Control	Atom % - Exposed to AO
C	77.7	24.6
O	17.2	50.2
Sn	0.8	10.1

Conclusions

It is clear that PETI-5 with boron carbide whiskers is the best combination of all the boron-containing samples tested. Compared to K3B, it has a higher compressive strength, a higher tensile strength, a higher maximum fiber stress, and a higher glass transition temperature. These properties are the result of the cross linking of the polymer chains which makes PETI-5 a thermoset. An added benefit is the relative ease with which void-free samples of PETI-5 can be made. It was difficult to make samples of K3B without voids.

We have shown that the addition of boron or a boron-containing compound to a polymeric material dramatically increases the utility of the material as a neutron shield. When boron carbide whiskers are used, the mechanical properties of the material are not significantly diminished. In fact, in some instances, they are significantly enhanced.

Long exposure to UV radiation does not appear to degrade any of the polymers studied, though the two thermoplastics, K3B and LaRC™-8515, do show some change on the surface as measured by XPS. Unfortunately, the UV irradiation apparatus broke down after our initial exposures so mechanical test specimens could not be run. Other bulk property measurements (TGA, TMA, and DMA) showed no change with UV exposure. This would suggest that mechanical properties would also be little changed.

The OPM experiment showed results similar to other experiments using the same materials. Unfortunately, the VUV measurements which might have shown how the surface was changing with time, were compromised by the collision and subsequent power failure. The test showed that the addition of BTO to a polymer film will reduce the erosion in the LEO by atomic oxygen. The film does become cloudy with AO exposure, however, so the optical proporties of the film will be diminished.

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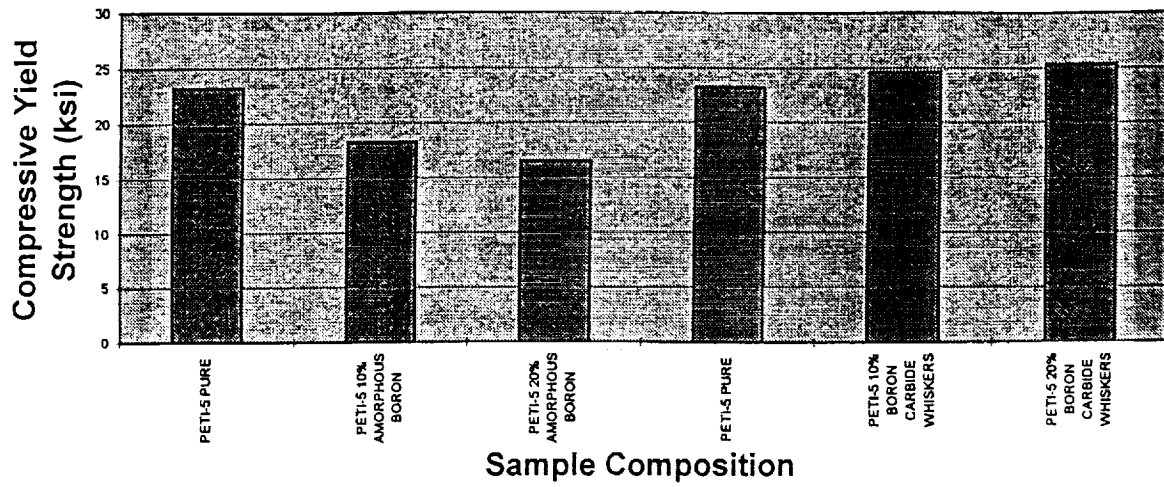
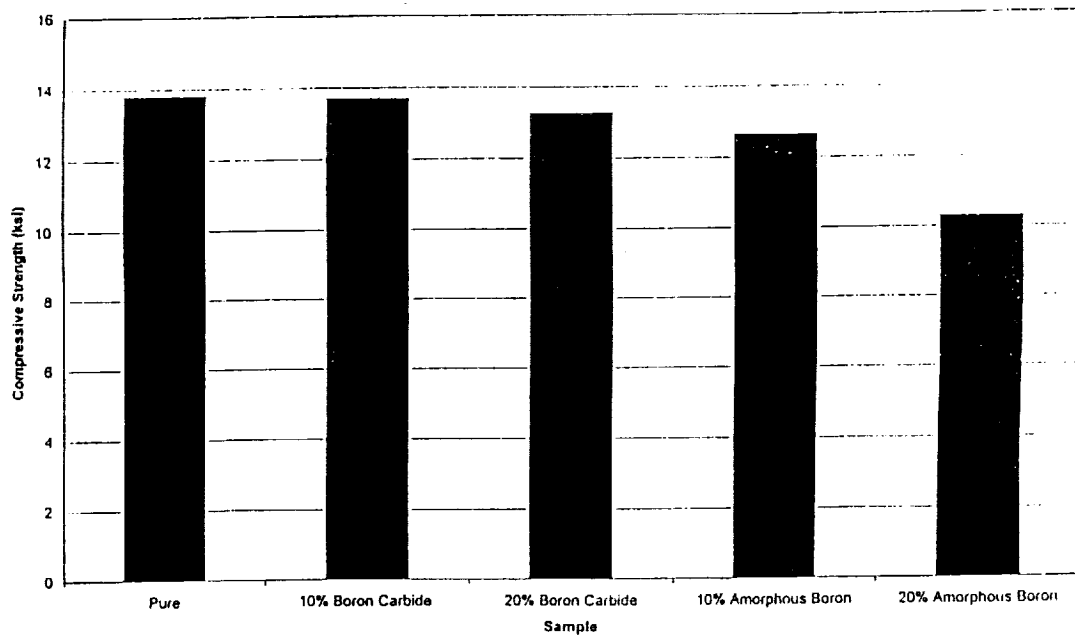Fig. 1   Compressive Strength of PETI-5 Materisals

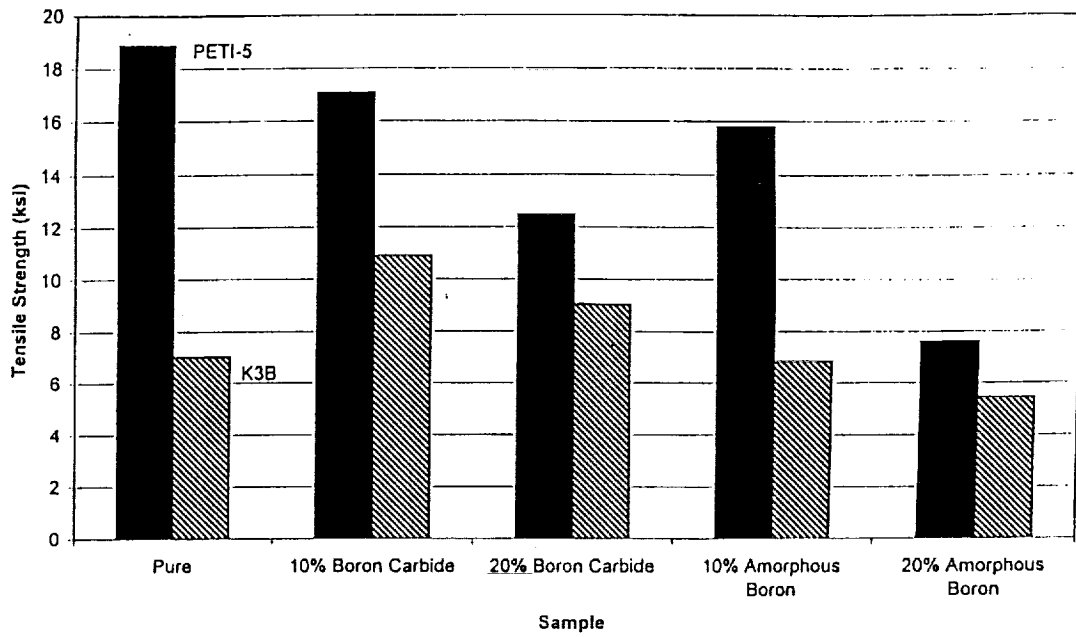Fig. 2   Compressive Strength of K3B Materials

Fig. 3   Tensile Strength of PETI-5 and K3B Materials
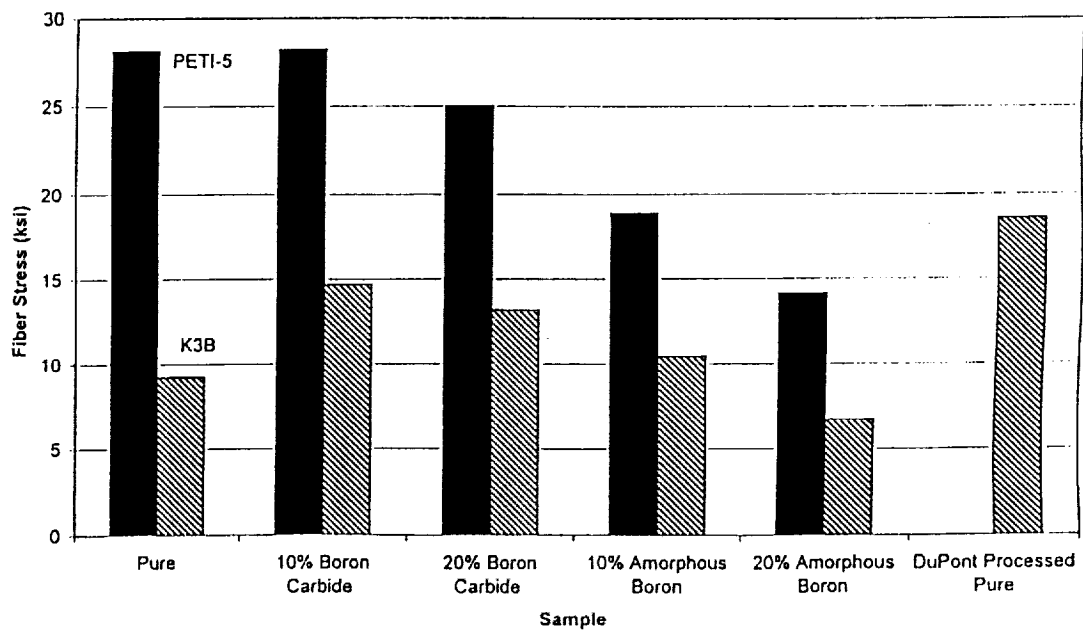

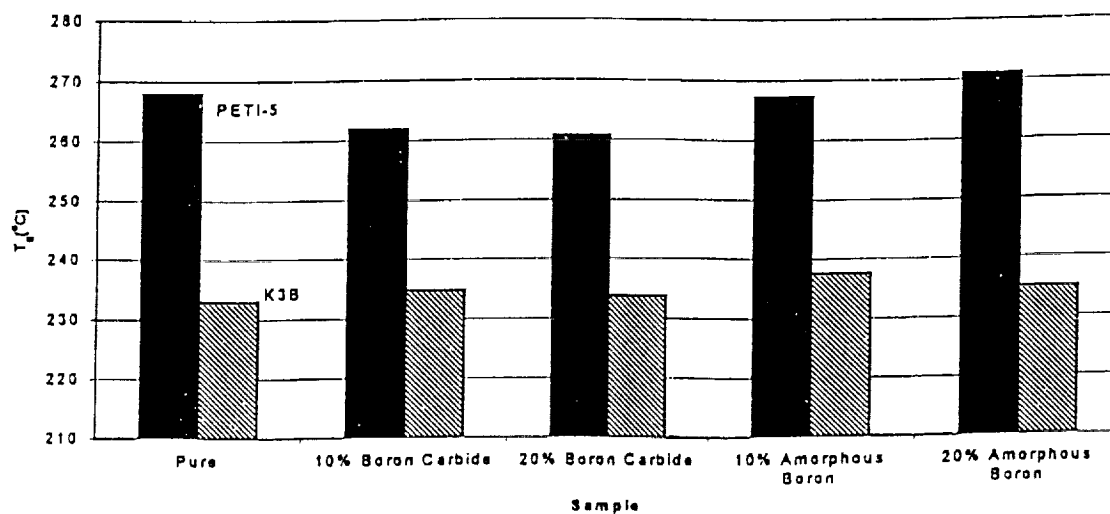Fig. 4   Maximum Fiber Strength for PETI-5 and K3B Materials

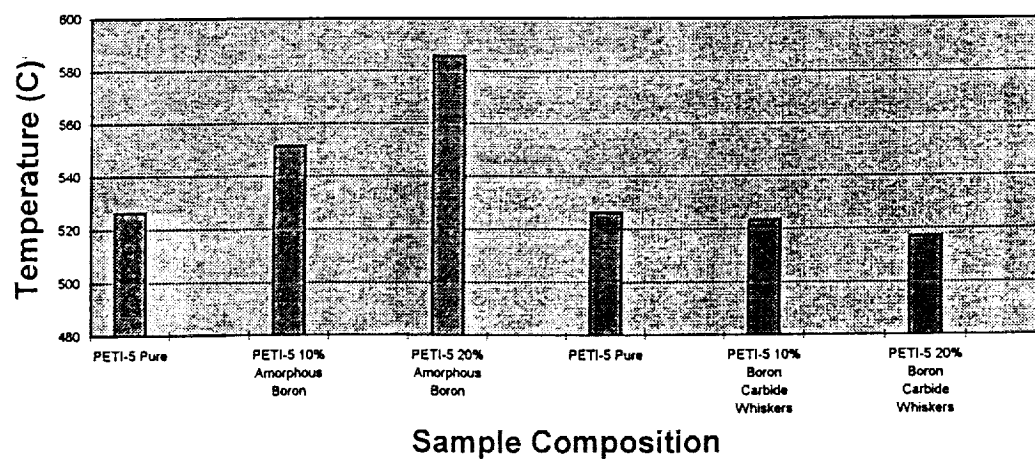Fig. 5 T_g for the PETI-5 and K3B Materials from DMA Data

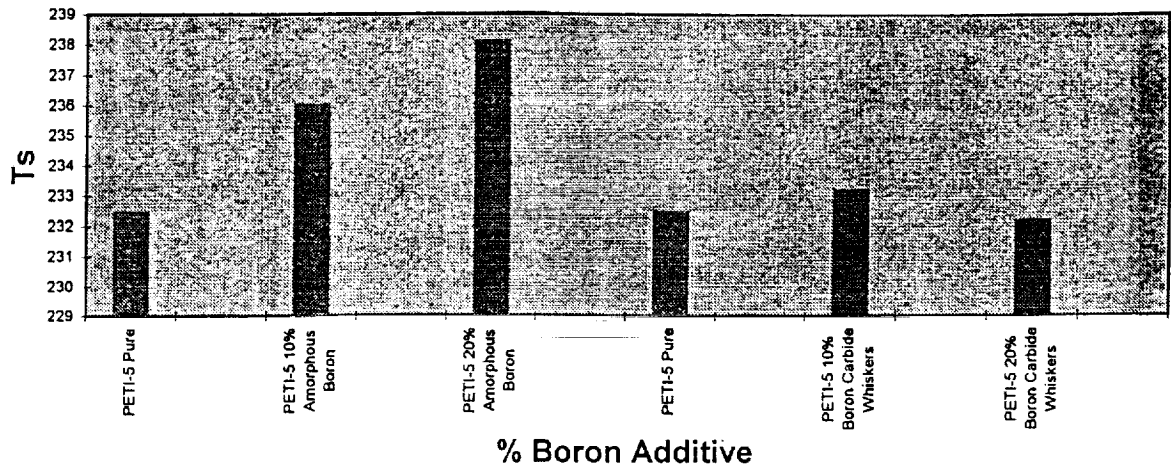Fig. 6   Temperature of 5% Mass Loss for PETI-5 from TGA Data

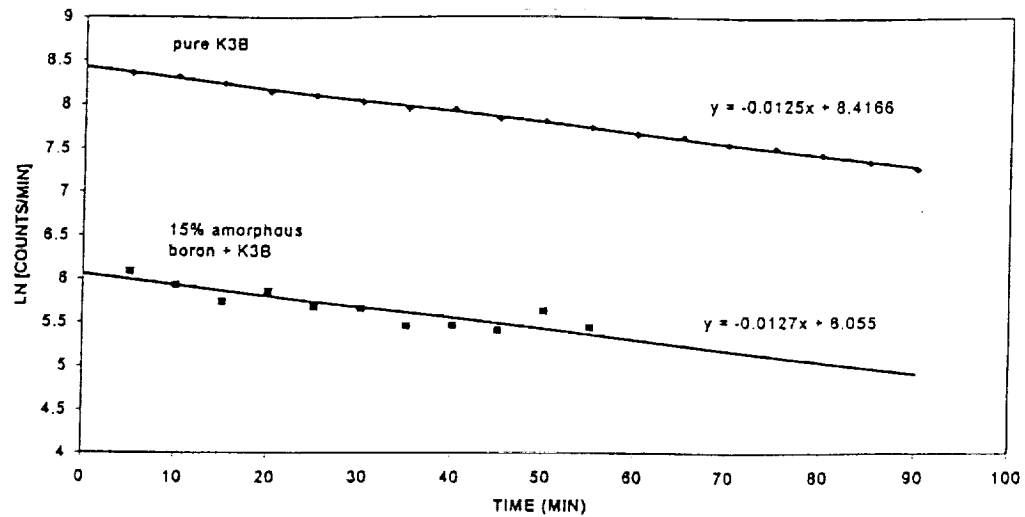Fig. 7 Softening Temperature, T_s, for PETI-5 from TMA Data

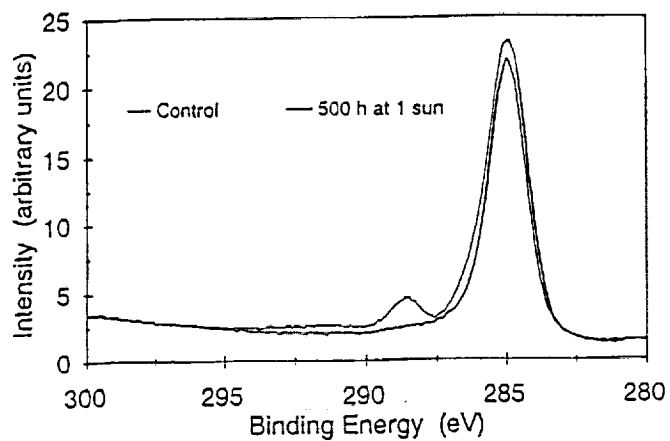Fig. 8 Activity of [116]In Produced Behind Pure K3B and K3B/15% Boron Powder

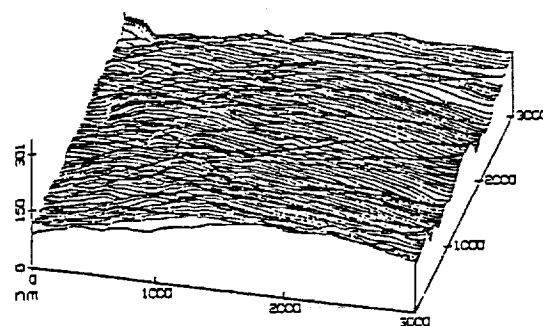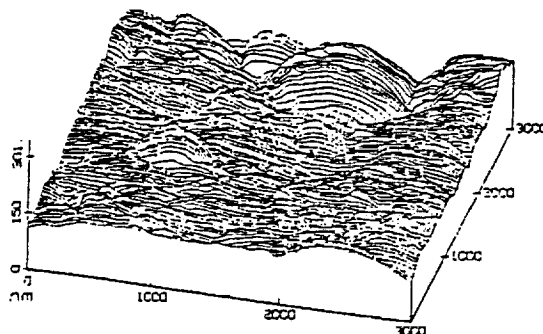Fig. 9 The XPS Spectrum for the Carbon 1s Peak of LaRC™-8515.

(A) Control

(B) Exposed to 1 sun for
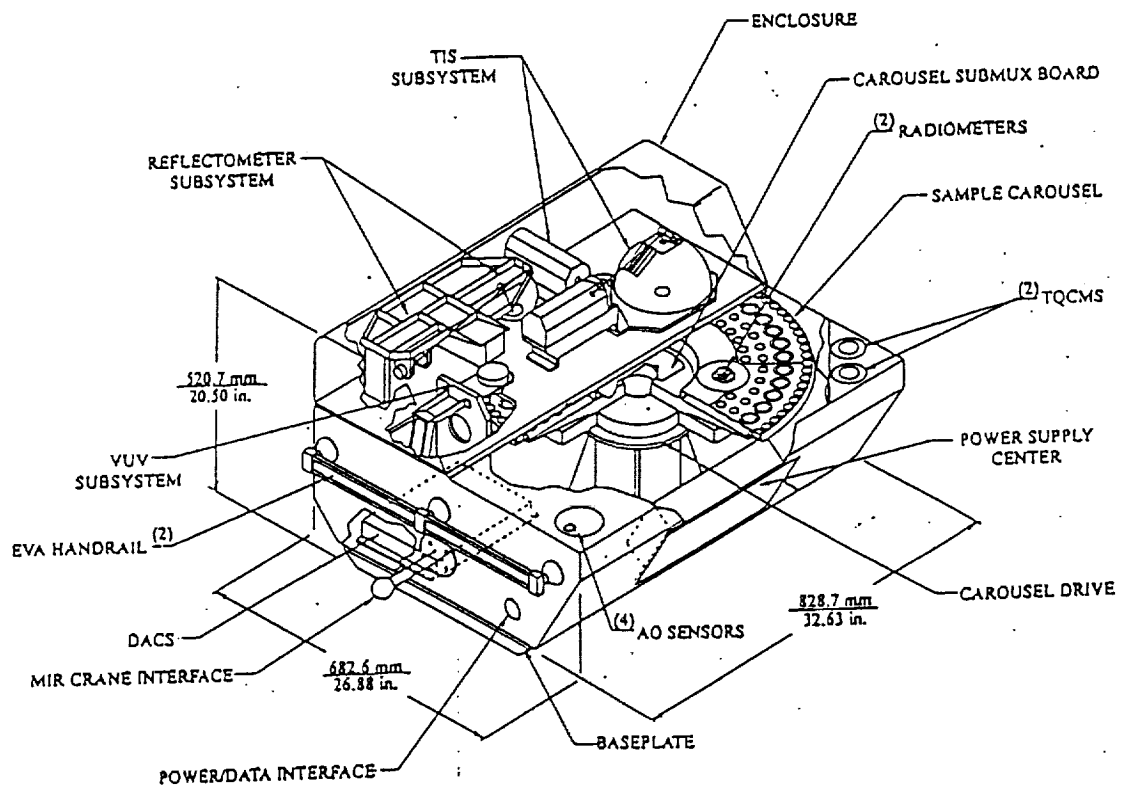500 hours at 177° C.

Fig. 10 Analysis of an IM7/K3B Specimen by AFM

Fig. 11   The Optical Properties Monitor Assembly